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**CALIBRATION OF DIATRON-20 RESIDUAL GAS ANALYZER
FOR USE IN HIGH VACUUM SYSTEMS**

by

S. V. Caruso

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ABSTRACT

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A method for calibrating a Diatron mass spectrometer is described in this report. The procedure is based on the diffusion of gases through a single polymer membrane (1/32-inch thick Teflon). The leak standard is first calibrated on an analytical mass spectrometer (CEC 21-620) in CC(STP)/sec for several gases. The apparatus then is used to determine the sensitivity of a Diatron mass spectrometer (CEC 133562) for the gases. This method provides a single leak rate standard for various gases. The reproducibility of replicate determinations is approximately ± 3 percent, which is within the limits of mass spectrometry techniques. In addition, the combination of the large membrane surface area and mechanism of gas diffusion through a polymer eliminates the problem of frequent plugging of microscopic orifice types of standards. This method also can be used for other gases that permeate a polymer diaphragm.

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SUMMARY

Rapid developments in ultra high vacuum techniques have brought about the need for more accurate low pressure measuring devices. In the current state of-the-art, mass spectrometers are being used to indicate residual gas pressure and to analyze volatile components in vacuum systems. However, since conventional sampling and calibrating methods are impractical in such systems, problems are encountered in obtaining accurate calibration of spectrometers.

A method for calibrating a Diatron mass spectrometer is described in this report. The procedure is based on the diffusion of gases through a single polymer membrane (1/32-inch thick Teflon). The leak standard is first calibrated on an analytical mass spectrometer (CEC 21-620) in CC(STP)/sec for several gases. The apparatus then is used to determine the sensitivity of a Diatron mass spectrometer (CEC 133562) for the gases. This method provides a single leak rate standard for various gases. The reproducibility of replicate determinations is approximately ± 3 percent, which is within the limits of mass spectrometry techniques. In addition, the combination of the large membrane surface area and mechanism of gas diffusion through a polymer eliminates the problem of frequent plugging of microscopic orifice types of standards. This method also can be used for other gases that permeate a polymer diaphragm.

INTRODUCTION

In ultra-high vacuum environmental studies, it has become necessary to identify qualitatively and to determine quantitatively the outgassing and evaporation products of selected materials. Because of the minute quantities of vapor evolved and the low pressure of the system, collection and transfer of a sample to an analytical instrument is not readily accomplished. Probably the most convenient arrangement is to utilize an analytical instrument which can be incorporated in the vacuum system. One instrument that will function in high vacuum and produce the desired analytical data is a mass spectrometer.

Currently, the radio frequency tube and the directional focusing type mass spectrometers are the most widely used devices for measuring partial pressures of residual gases in vacuum systems. This laboratory has obtained a Consolidated Electrodynamics Corporation Model 133562 (Diatron) mass spectrometer. The Diatron spectrometer is a small electronic instrument capable of measuring extremely small amounts of gases and volatile liquids. The components are comprised of the analyzing cycloid tube, magnet, auxiliary electronics, and a Leeds and Northrup recorder. A detailed description of theory, operation, and maintenance can be obtained from the instrument manual (Reference 1). The following is a general description of the specifications and capabilities as given by the manufacturer.

The Diatron assembly consists of a 180° -focusing tube with the ion source and analyzer combined in a single envelope; a removable permanent Alnico V magnet rated at 4000 gauss also is included. The output signal has seven attenuation ranges: X1, X3, X10, X30, X100, X300, and X1000. The scanning dial covers the mass range from 10 to 80 in one revolution and is calibrated to read directly in mass (m/e) units. A switch for low mass is provided for scanning m/e values of 2 to 10. Scanning can be done automatically or manually. Peaks can be resolved to mass 32 with less than 1 percent contribution from adjacent masses. The amplifier indicates 5×10^{-13} amperes full scale on the X1 range, and the ionization current is adjustable from

20 to 100 microamperes. Operational pressure of the tube is 1×10^{-4} mm Hg or less. The analyzer will detect partial pressures of 1×10^{-9} mm Hg for most gases in the mass range of the instrument. The magnet can be removed and the Diatron envelope baked to 450°C . The entire assembly is shown in FIG 1.

In order to derive analytical data from the instrument, the signal output for known quantities of gases must be calibrated. Qualitative calibration is not necessary since m/e values of 2 to 80 are indicated directly. However, partial pressure (quantity) measurements can be made only when the sensitivity for each (m/e) value is known. The sensitivity factors for each m/e value are characteristic of the individual instrument and must be determined for the system in which it is used. This is computed for each gas by dividing the base peak height (chart divisions) by the pressure (microns). From the sensitivity factor, the partial pressure of a gas can be calculated.

The following formula expresses the manner by which masses are resolved in the analyzing tube:

$$R = \sqrt{\frac{2E(m/e)}{B^2}} \quad (1)$$

where:

R = Radius of curvature of (m/e) travel in cm

E = Accelerator voltage potential

$m/e = \frac{\text{Mass number (grams)}}{\text{Number of electrons lost}}$

B = Magnetic field strength in gauss

Each positively ionized mass is brought into focus on a fixed-position target collector by varying the accelerator voltage current. The electron current produced on the collector by the positively ionized gases is amplified and recorded as peak heights on a strip-chart recorder. Once determined, the sensitivity for each m/e value will

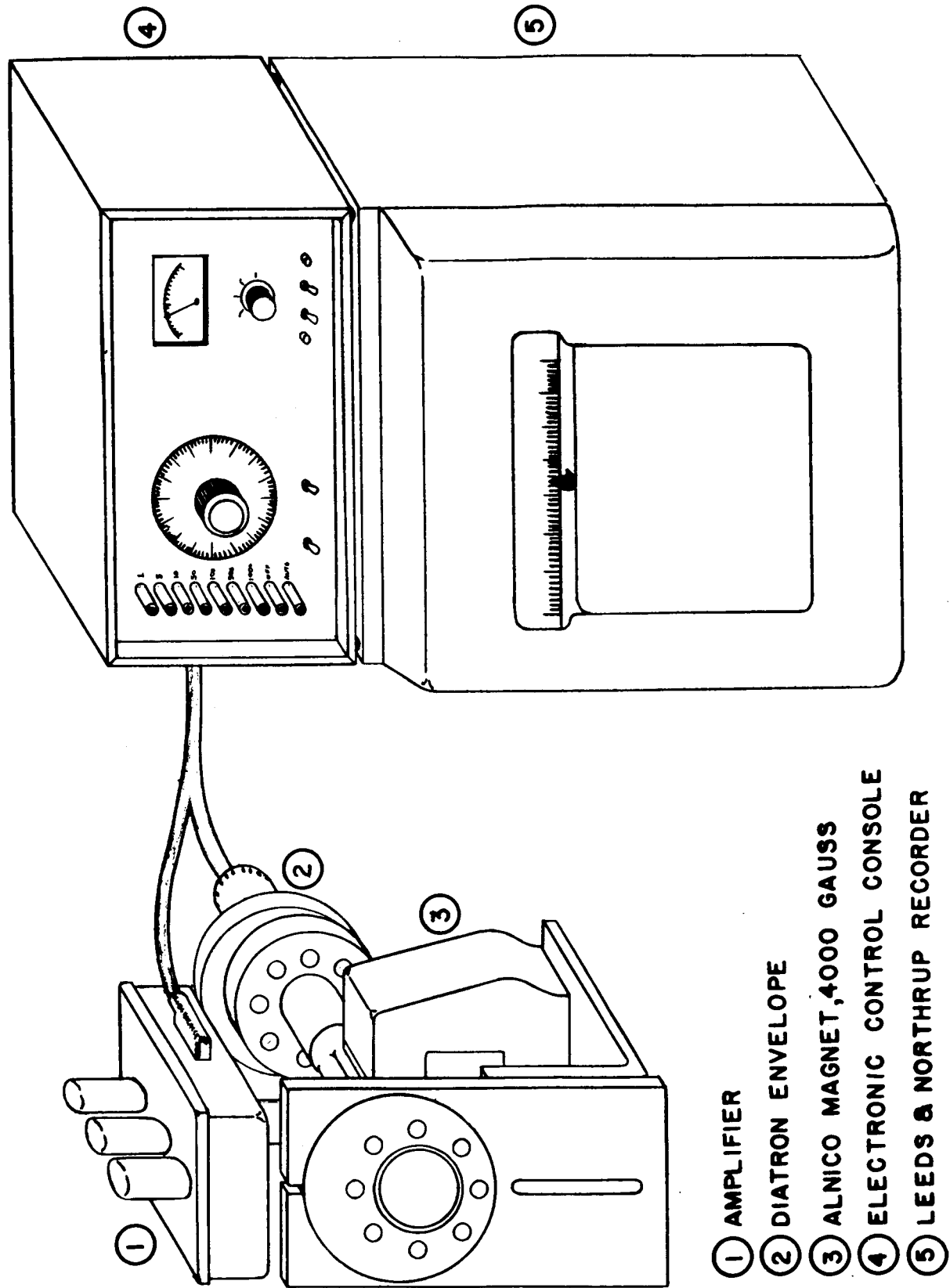


FIGURE 1. DIATRON ASSEMBLY, CONTROLLER AND RECORDER

not vary appreciably. However, changes in ionizing current and temperature of the gas and Diatron tube will affect the sensitivity and must be kept constant. As is the case with all mass spectrometers, periodic recalibration is mandatory because of the aging of electronic components.

The conventional method for calibrating a mass spectrometer may be described briefly as follows. The gas is introduced into a sample inlet chamber and measured with a mercury manometer in millimeters. A known volume of the sample is expanded 1000 times. At this point, a micromanometer may be used for more precise pressure measurement. The expansion volume is sufficiently large (normally 3 liters) to provide an essentially constant sample pressure during the time required for analysis. The gas is then introduced into the analyzing chamber through a gold leak diaphragm and the mass spectrum recorded.

The incorporation of a mass spectrometer in ultra high vacuum systems is quite common. For a clean, empty system, identification of residual gases has generally been sufficient for most applications. However, for studying the effects of vacuum on materials, it is necessary to quantitatively analyze the components evolved at the reduced pressure. Quantitative calibration of mass spectrometers in such applications is difficult because of the impracticability of providing a standard gold leak orifice and sample inlet chamber. The method currently used by most investigators requires the use of a preformed mechanical leak that has been calibrated for a given gas. This approach is sometimes accurate, but usually is limited to a single gas. Instruments that provide variable leak rates are commercially available; but the accuracy of such devices tested in this laboratory generally has been no better than ± 20 percent. Preformed leaks, produced in the laboratory from glass capillary tubing, decreased gradually until the flow of gas stopped completely. Oak Ridge Laboratory Y-12 reported (Reference 2) that the accuracy of their glass standards was ± 11 percent. However, these standards required frequent recalibration because of a continuous decrease in the leak rate.

DIATRON MODEL 133562 MASS SPECTROMETER

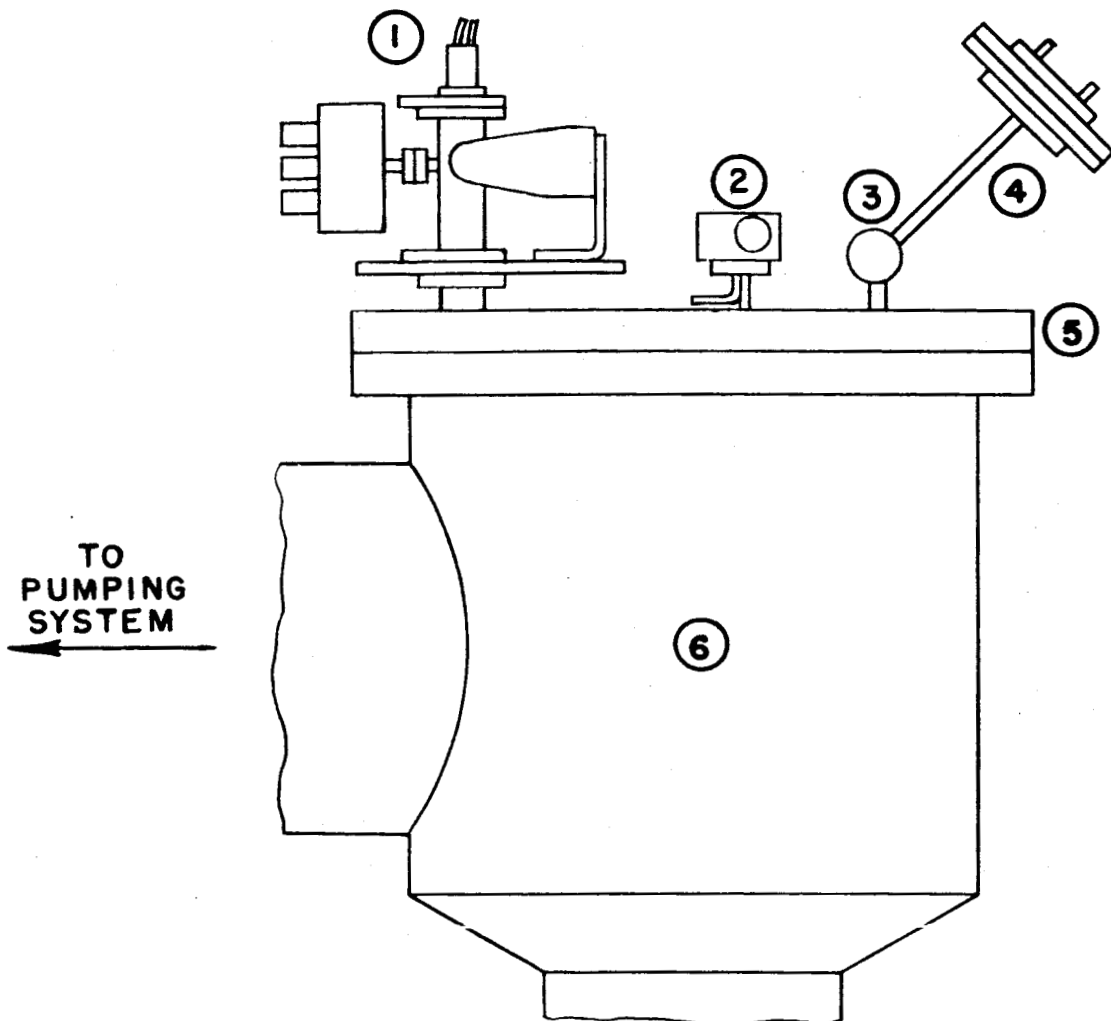
The Diatron assembly was installed on an ultra-high vacuum system capable of achieving a pressure of 10^{-10} mm Hg. This arrangement is shown in FIG 2. A flat plate (5) (1-inch thick by 18-inch diameter) was fabricated to fit the bottom half of the vacuum chamber. Welded onto the plate were the Diatron envelope flange (1), a Granville-Phillips variable leak control (2), and a 0.5-inch diameter steel tube two inches in length and having a wall thickness of 1/16 inch and an attached flange (3). The flange permitted coupling of auxiliary apparatus to the system. With the Diatron in this position, the analyzing tube was exposed to the same conditions of pressure as the vacuum chamber. With the Diatron magnet removed, the entire system was baked out to 450°C.

A mass spectrum recorded during pump-down of the empty system indicated that at least twenty-four hours were required to reach a constant pressure (designated as the system blank). The mass peaks recorded in the blank are shown in Table 1.

Table 1. Spectrum Blank for the System

m/e Detected	Probable Identity	Peak Height, Chart Divisions
14	N	1
18	H ₂ O	10
28	N ₂ and/or CO	4

A sensitivity calibration of the tube was undertaken for several gases. The process of continuous pumping of an open chamber with the current equipment prohibited calibration by the batch sample method. An alternative was to provide a known gas leak rate into the system. There are two methods of calibrating the Diatron in this manner; the first is to use a variable leak valve and accurately measure the total pressure with an ion gauge; the other is to have



- ① DIATRON ASSEMBLY
- ② VARIABLE LEAK CONTROL
- ③ FLANGE ADAPTER
- ④ STANDARD LEAK RATE APPARATUS
- ⑤ 1 INCH THICK VACUUM CHAMBER COVER PLATE
- ⑥ HIGH VACUUM CHAMBER

FIGURE 2. DIATRON ASSEMBLY INSTALLED ON HIGH VACUUM CHAMBER

the leak-rate apparatus pre-calibrated for one or more gases, which will then be used as a standard for the Diatron. Each of these methods was used in attempts to calibrate the Diatron. The first method involved the use of a Granville-Phillips Company variable leak control and an ionization gauge as the primary standard for measuring the total pressure of the system; the gas container was attached to the inlet of the variable leak. This method proved unsuccessful because the reproducibility of the leak rate was no better than ± 20 percent and the sensitivity of the ionization gauge for the gases was not known. The alternate method was the design of an apparatus which permitted the leak rate for different gases to be found prior to calibrating the Diatron tube. This approach proved successful and is described in the following section.

PRIMARY STANDARD CALIBRATION APPARATUS

The principle used in producing a single standard leak for use with different masses was based on the permeation and diffusion of gases through a membrane. When a differential pressure exists on a material, gas will permeate from the high pressure side, diffuse slowly through the material, and be given up on the low pressure side. Upon saturation of the material, the gas flow rate becomes constant (Reference 3). The diffusion rate (D) is usually expressed in the following terms:

$$D = \frac{Q}{T \cdot A \cdot M \cdot P}$$

D = Diffusion rate

Q = CC gas at S. T. P.

T = Time in seconds

A = Surface area in square centimeters

M = Thickness of material in millimeters

P = Millimeters mercury differential pressure on material

An apparatus that had been used previously to study the diffusion of gases through metals and plastics (Reference 4) was selected for this investigation and is shown in FIGS 3 and 4. The exploded view in FIG 4 illustrates the position in which a diaphragm of the selected material is placed. The entire apparatus is attached to a CEC Model 21-620 analytical mass spectrometer (not the Diatron) for calibration. A pressure of one atmosphere is applied to one side of the diaphragm, and the mass spectrometer provides a pressure of approximately 10^{-5} mm Hg on the other side. The calibrating gas is passed over the diaphragm as shown in FIG 3.

A polymer diaphragm was selected as the material to provide a standard leak. The mechanism of diffusion of gases (other than monatomic) through organic solids differs from that of metals. With polymers, gases penetrate the material as molecules, whereas with metals the gases dissociate prior to diffusion. The rate of permeation of gases through organic materials varies directly with pressure as shown by the formula (References 5 and 6):

$$q = DAh \frac{(P_1 - P_2)}{d} t$$

where:

q = Total amount of materials permeating a membrane

D = Diffusion coefficient

A = Surface area of diaphragm

t = Time

h = Solubility of gas in material

P_1 = Gas pressure on high side

P_2 = Gas pressure on low side

d = Thickness

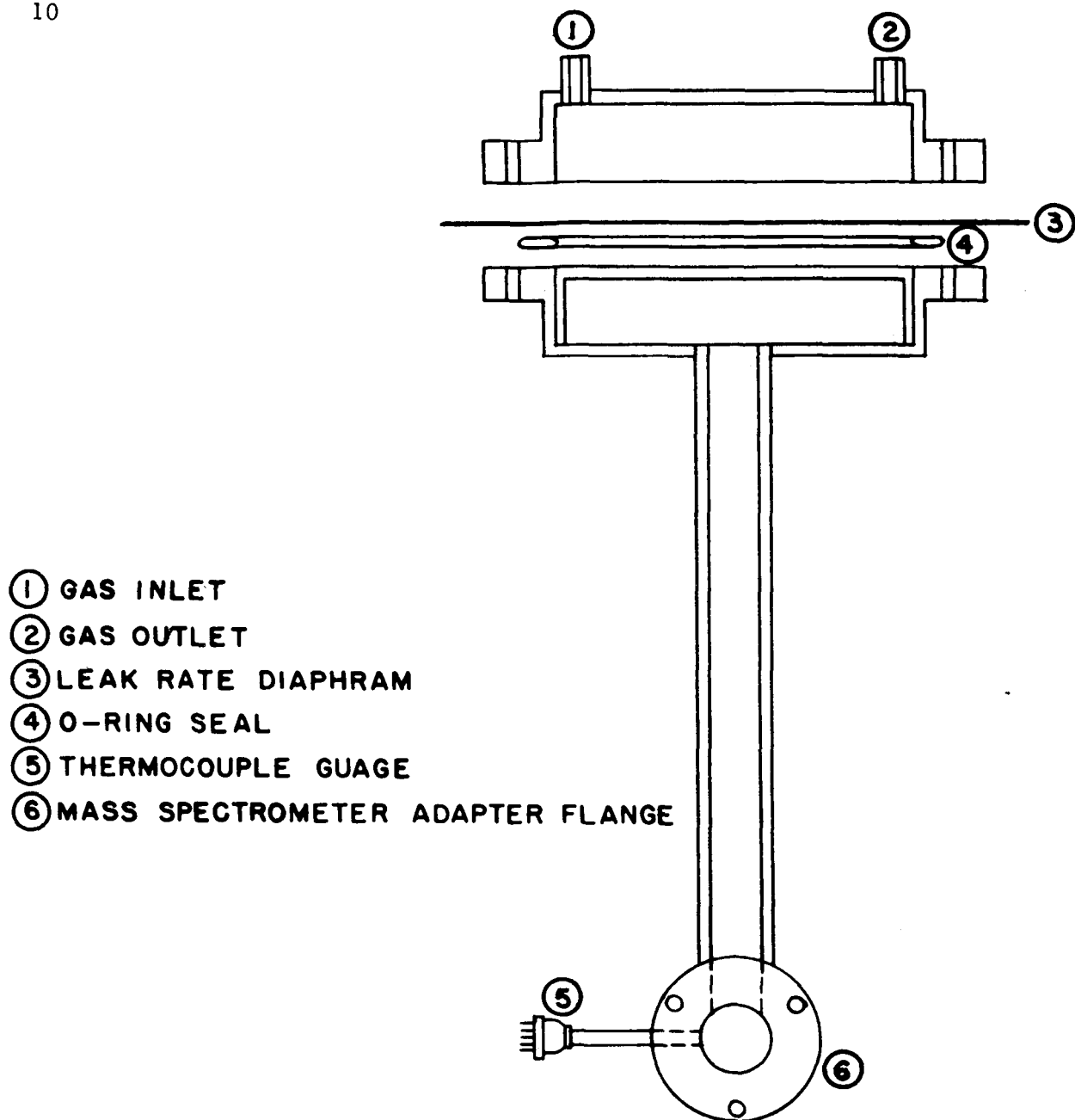


FIGURE 3. SIDE VIEW OF LEAK RATE STANDARD APPARATUS

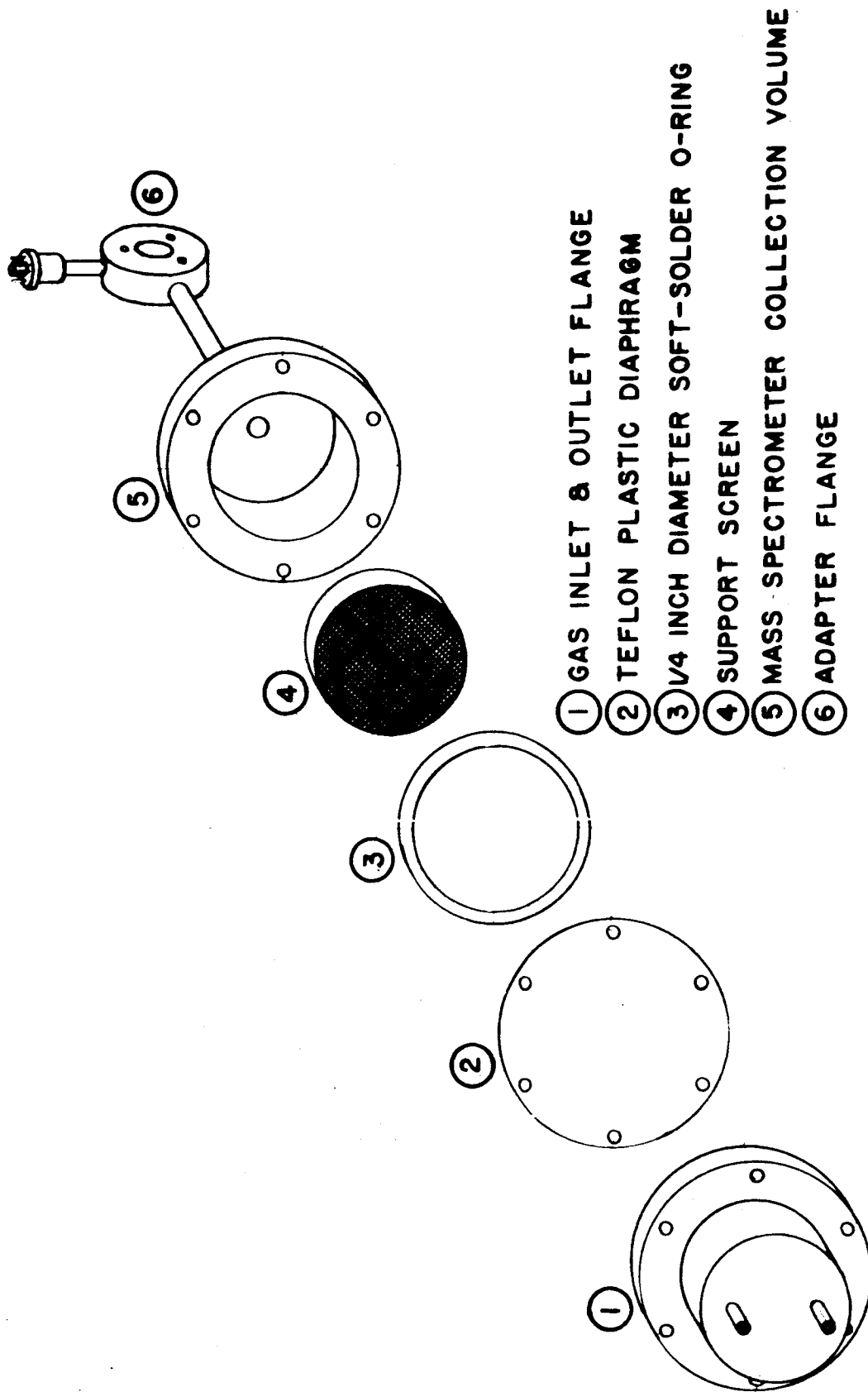


FIGURE 4. EXPLODED VIEW OF LEAK RATE STANDARD APPARATUS

A Teflon-TFE diaphragm (1/32-inch thick) was chosen as the material to serve as the leak rate standard. Previous studies had shown the diffusion rates of gases through this polymer to be large enough to be detected by the Diatron, yet not large enough to increase appreciably the pressure in the vacuum system.

Calibration consisted of three separate operations. The first was calibration of a CEC analytical mass spectrometer. The second was determination of the leak rate for hydrogen, helium, oxygen, and nitrogen through the diaphragm using the CEC analytical mass spectrometer. The third consisted of using the calibrated leak for calibration of the Diatron in the actual vacuum system. Details of these procedures are as follows:

1. Calibration of the Analytical Mass Spectrometer

A model CEC 21-620 mass spectrometer was calibrated for sensitivity to hydrogen, helium, oxygen, and nitrogen by use of the instrument's batch inlet system and expansion volume. The sensitivity factors are given in Table 2.

Table 2. Calibration of CEC Model 21-620 Analytical Mass Spectrometer

Gas	m/e	Sensitivity Div. /Micron Pressure
H ₂	2	48.3
He	4	18.3
O ₂	32	161.9
N ₂	28	217.9

After calibration of the mass spectrometer, the expansion chamber was replaced with the diffusion apparatus (FIG 5).

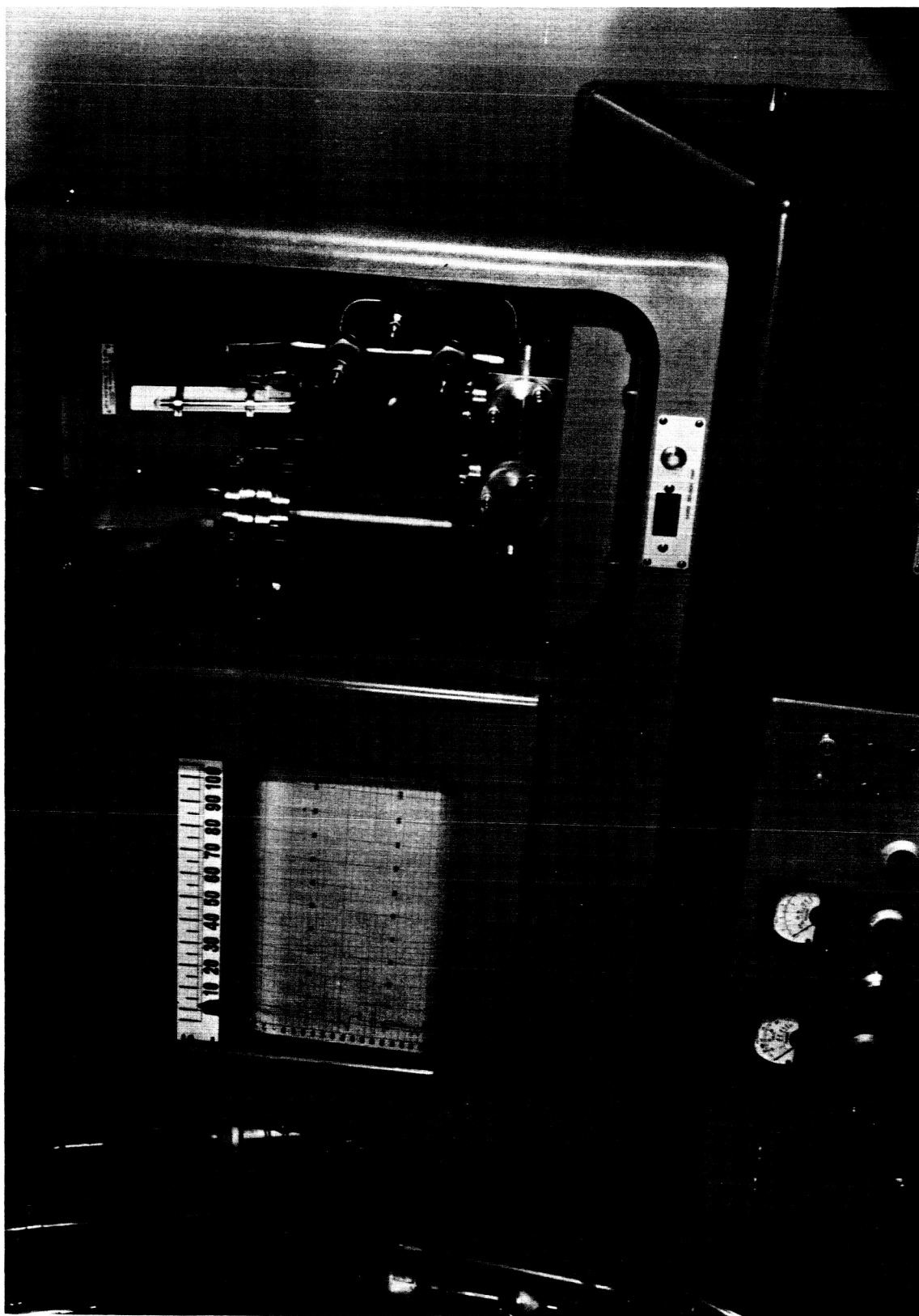


FIGURE 5. MASS SPECTROMETER USED TO CALIBRATE LEAK RATE STANDARD

2. Calibration of Standard Leak

Hydrogen and helium gas were obtained from compressed gas cylinders. Nitrogen and oxygen were obtained from the laboratory air pressure supply. In either event, the gas container was attached to the inlet side of the diffusion apparatus, the gas was passed over the diaphragm, and exhausted through the outlet tube (FIG 3). Each gas, monitored for impurities, was allowed to permeate the membrane for at least twenty-four hours before a sample for calibration was collected. This provided ample time for impurities to completely desorb from the Teflon. To insure that the gas was diffusing only through the diaphragm, a plastic bag was put around the diffusion apparatus and a helium atmosphere maintained inside the bag. This arrangement provided a constant check for leaks that might occur around the connecting flanges during nitrogen and oxygen measurements. Thus, as long as helium was not detected in the collection sample, it was known that only diffusion through the diaphragm had occurred. During helium calibration, nitrogen gas was used in the plastic bag for the leak check.

A gas sample of known volume was collected during a timed interval from the low pressure side of the diaphragm. An adequate sample, as indicated by the pressure increase, was collected in three minutes or less. The sample then was pumped into the cycloid tube and quantitatively analyzed. The diffusion rates were determined directly as chart divisions/micron gas pressure/sec and converted to CC (STP)/sec by use of the spectrometer sensitivity factors. The total leak rate of the whole diaphragm surface area was the only factor required.

3. The Diatron and Ultra-High Vacuum System

FIG 2 shows the ultra-high vacuum system with the Diatron tube assembly installed. The flange to which the diffusion leak rate standard is attached is a duplicate of the one on the CEC 21-620 analytical mass spectrometer. This arrangement facilitated interchange of attachments between the two instruments and permitted the leak rate standard to be transferred without disturbing the diaphragm and seal.

Prior to installation of the apparatus on the vacuum system, the flange (3), FIG 2, was blinded and the system pumped down to the

minimum pressure which could be obtained without baking. A spectrum was made of the residual gases at the lowest obtainable pressure for use as a blank (Table 1).

After attaching the diffusion leak rate standard to the vacuum system, the calibrating gas was supplied to the diaphragm in the same manner as previously described for the analytical mass spectrometer, and the Diatron tube was calibrated for its sensitivity to a continuous flow rate for each gas. The Diatron output from the standard leak was recorded in chart divisions and the sensitivities were computed in the units, CC (STP)/sec/division. A plastic bag and helium gas were used for checking leakage during calibration.

Calculations

Several calculations are involved in the calibration of the standard leak apparatus and the Diatron tube. Initially, the CEC analytical mass spectrometer was calibrated for sensitivity to each gas. This value for each m/e (gas) was computed as chart divisions/micron pressure (Table 2). With the diffusion apparatus attached to the spectrometer, measurements were taken as divisions/second for the rate at which a gas diffused through the diaphragm. The leak rate then was expressed as follows:

$$\frac{\frac{D}{S}}{\frac{d}{\mu}} = C$$

where:

D = Chart divisions derived from the spectrum of the calibrating gas

S = Time in seconds for total sample collection of the gas (m/e)

$\frac{d}{\mu}$ = Sensitivity factor for the gas as chart divisions/micron gas pressure

C = Diaphragm total leak rate in microns pressure/second

The pressure, in microns, for each gas was converted to a leak rate in CC(STP) / second. Table 3 gives the computed values for the leak rate for hydrogen, helium, oxygen, and nitrogen.

Table 3. Analytical Mass Spectrometer Calibration
of Teflon Diaphragm Leak Rate for Four Gases

Diaphragm - 4-Inch Diameter, 0.03 Inch Thick at 26°C				
Gas	m/e	Divisions/ Second	Leak Rate CC(STP)/sec	Percent Average Deviation*
Hydrogen	2	3.65	2.14×10^{-5}	± 1.8
Helium	4	7.59	5.17×10^{-5}	± 2.0
Nitrogen	28	4.33	2.72×10^{-6}	± 2.6
Oxygen	32	2.32	1.98×10^{-6}	± 2.7
*Based on 6 to 11 determinations.				

Calibration Sensitivites

The time needed for the calibration of each gas was approximately four days. Readings were taken each day. Reproducibility was determined by calibrating each gas several times.

With the apparatus attached to the Diatron assembly, readings were taken for each of the four gases. Table 4 gives the sensitivity factors of the Diatron tube for the gases tested.

Table 4. Diatron Sensitivity for Hydrogen, Helium, Nitrogen, and Oxygen at 26°C

Gas	m/e	Sensitivity Factor CC (STP)/sec/div
Hydrogen	2	2.58×10^{-7}
Helium	4	5.28×10^{-7}
Nitrogen	28	6.63×10^{-8}
Oxygen	32	1.10×10^{-7}

OTHER APPLICATIONS

Although this investigation was limited to the determination of the sensitivity of the Diatron for hydrogen, helium, nitrogen, and oxygen, the procedure is applicable for other gases as well.

Determining the sensitivity of the Diatron for non-gaseous materials is also possible, but requires a different procedure. The complexity of the mass spectrum obtained from some liquids and solids requires a detailed study for each material. However, the sensitivity of the Diatron for selected liquids and solids can be investigated by placing a sample of the material in a special holder, attaching the sample chamber to the vacuum system, allowing the material to evaporate, and obtaining a mass spectrum from the resulting vapors. From these data, together with the known rate of evaporation of the material, the sensitivity of the Diatron for that material can be calculated.

CONCLUSIONS

The production and calibration of a single standard leak mechanism for different masses have been carried out by utilizing the diffusion of gases through a membrane. All gases diffuse through polymers to some extent, depending on the solubility of the gas in the polymeric material. The diffusion rate is measurable at ambient temperature with reasonably thick membranes (.1 inch and less). Also, polymers are easily fabricated to a desired thickness. Teflon-TFE (1/32-inch sheet) provided leak rates within the calibrating range of the Diatron mass spectrometer and proved to be well suited for this application.

The diffusion apparatus has several advantages for use as a primary standard leak. The diaphragm may be calibrated with an analytical mass spectrometer, which is the most accurate, partial pressure measuring instrument available. The large surface area of the membrane minimizes the effect of possible particulate contamination. In addition, gases permeate the polymer and do not depend on micro-leaks that easily become stopped up. Although changes in temperature cause the diffusion coefficient to vary, the experimental work can be carried out at a controlled temperature so that this possible source of difficulty is circumvented.

The main disadvantage of the diffusion method is the time required for precalibration of the leak rate standard. Each gas must be calibrated separately, and the time required for each gas is approximately four days. However, the accuracy and reproducibility derived by this method justifies the time element involved.

Two other procedures were investigated in an attempt to produce a single standard leak for different gases. One method involved the use of a variable micro-leak valve and an ionization gauge for pressure measurement. With this arrangement, the reproducibility of leak rates for consecutive runs was ± 20 percent. The second method involved fabrication of a fixed rate leak using a glass capillary. Preliminary testing on a Veeco helium leak detector showed this apparatus to be impractical since the helium flow gradually decreased and finally ceased. This effect occurred with each glass capillary produced in the laboratory.

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APPROVAL

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The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.



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